

NEAR-INFRARED ABSORPTION FILM

CROSS REFERENCE TO RELATED APPLICATION

[0001] This is a continuation application of
5 PCT/JP02/10252 filed on October 2, 2002.

FIELD OF THE INVENTION

[0002] The present invention relates to a near-infrared
absorption film.

10

BACKGROUND OF THE INVENTION

[0003] In an electromagnetic-wave shielding and light
transmitting plate used as a front filter of a PDP (plasma
display panel), a near-infrared absorption film may be
15 attached to the electromagnetic-wave shielding and light
transmitting plate at the PDP side. The near-infrared
absorption film absorbs near-infrared absorption rays
introducing errors of other peripheral electronics devices.
As conventional near-infrared absorption films, there are
20 a filter made of phosphate glass containing metallic ion such
as copper or iron; an interference filter which is obtained
by forming layers having different refractive indexes on a
substrate and allows the transmission of specific
wavelengths by interfering with transmitting lights; an
25 acrylic resin filter containing copper ion; a filter obtained
by dispersing a dye into polymer; and the like.

[0004] As for the near-infrared absorption film obtained
by dispersing a dye into polymer, the near-infrared
absorption property of filter becomes poor as the dye is
30 deteriorated by heat, oxidation, or the like.

DISCLOSURE OF THE INVENTION

[0005] A near-infrared absorption film of the present invention has a base film and a near-infrared absorption layer formed on the base film, and is characterized in that the near-infrared absorption layer contains a diimmonium compound which has an endothermic peak of 220°C or more, determined from differential scanning calorimetry (DSC measurement) with temperature rising rate of 10°C/minute.

5

DETAILED DESCRIPTION

[0006] A near-infrared absorption film has a base film and a near-infrared absorption layer formed on the base film and may further have another layer.

[0007] The near-infrared absorption layer contains a diimmonium compound and may further contain another component.

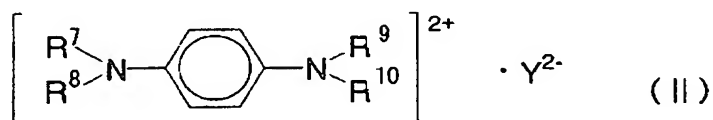
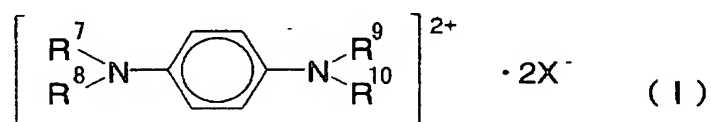
[0008] The diimmonium compound has endothermic peak of 220°C or more, determined from differential scanning calorimetry (DSC measurement) with temperature rising rate of 10°C/minute. This diimmonium compound has high degree of purity so as to improve the durability of the near-infrared absorption film.

[0009] The diimmonium compound preferably has endothermic peak of 225°C or more, more preferably from 225°C to 240°C, determined from the differential scanning calorimetry (DSC measurement) with temperature rising rate of 10°C/minute.

[0010] The differential scanning calorimetry (DSC measurement) is a method of measuring, as a temperature function, differences in energy input between a measurement

objective material and a reference material while the temperature was changed according to program by means of a heat flow DSC calorimeter. The temperature at endothermic peak indicate a temperature (melting point) at an intersection point of tangential lines drawn at the maximum inclinations on both sides of the endothermic peak.

[0011] The diimmonium compound is preferably a compound represented by the following formula (I) or (II):

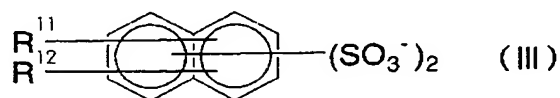


[0012] In the formulae (I) and (II), each of R^7 through R^{10} is at least one of an alkyl group, an aryl group, a group having aromatic ring, a hydrogen atom, and a halogen atom, X^- is a monovalent anion, and Y^{2-} is a divalent anion.

[0013] The monovalent anion represented by X^- may be a halogen ion such as I^- , Cl^- , Br^- , or F^- ; an inorganic acid ion such as NO_3^- , BF_4^- , PF_6^- , ClO_4^- , or SbF_6^- ; an organic carboxylic acid ion such as CH_3COO^- , CF_3COO^- , or benzoic acid ion; an organic sulfonic acid ion such as $CH_3SO_3^-$, $CF_3SO_3^-$, benzenesulfonic acid ion, or naphthalenesulfonic acid ion.

[0014] The divalent anion represented by Y^{2-} is preferably an aromatic disulfonic acid ion having two sulfonic acid

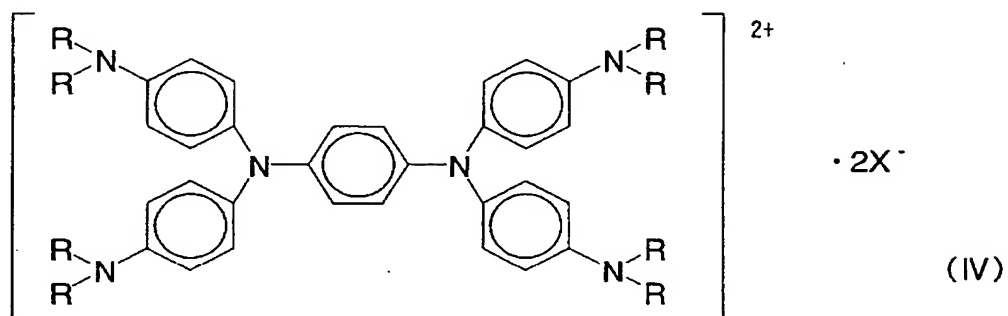
groups. Specific examples are an ion of naphthalenedisulfonic acid derivatives such as naphthalene-1,5-disulfonic acid, R acid, G acid, H acid, benzoyl H acid (a benzoyl group being attached to an amino group of H acid), p-chlorobenzoyl H acid, p-toluenesulfonyl H acid, chloro H acid (an amino group of H acid being replaced with a chlorine atom), chloroacetyl H acid, metanyl γ acid, 6-sulfonaphthyl- γ acid, C acid, ϵ acid, p-toluenesulfonyl R acid, naphthalene-1,6-disulfonic acid or 1-naphthol-4,8-disulfonic acid; carbonyl J acid, 4,4-diaminostilbene-2,2'-disulfonic acid, di-J acid, naphthalic acid, naphthalene-2,3-dicarboxylic acid, diphenic acid, stilbene-4,4'-dicarboxylic acid, 6-sulfo-2-oxy-3-naphthoic acid, anthraquinone-1,8-disulfonic acid, 1,6-diaminoanthraquinone-2,7-disulfonic acid, 2-(4-sulfophenyl)-6-aminobenzotriazole-5-sulfonic acid, 6-(3-methyl-5-pyrazolonyl)-naphthalene-1,3-disulfonic acid, 1-naphthol-6-(4-amino-3-sulfo)anilino-3-sulfonic acid, and the like. Among these, a naphthalenedisulfonic acid ion is preferable and a naphthalenedisulfonic acid ion represented by the following formula (III) is especially preferable:



[0015] In the formula (III), each of R^{11} and R^{12} is at least one selected from a group consisting of a lower alkyl group, a hydroxyl group, an alkylamino group, an amino group, -NHCOR^{13} , $\text{-NHSO}_2 R^{13}$, $\text{-OSO}_2 R^{13}$ (where R^{13} is at least one selected from

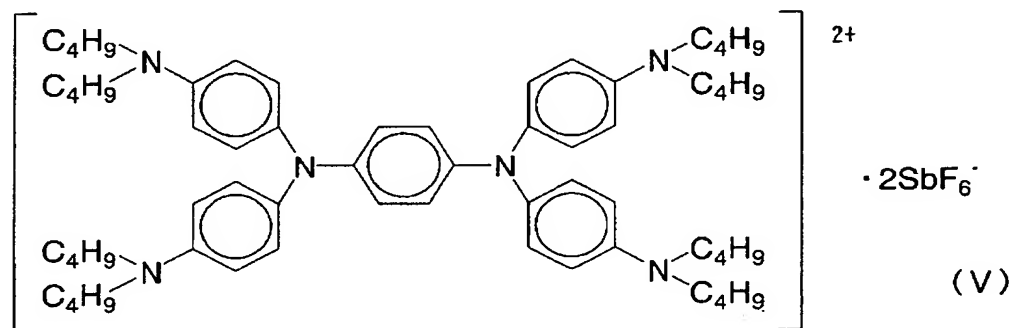
a group consisting of aryl groups and alkyl groups, R^{13} may have substituent(s)), an acetyl group, a hydrogen atom, or a halogen atom.

[0016] A suitable example of the diimmonium compound is represented by the following formula (IV):



[0017] In the formula (IV), R is an alkyl group having 1 to 8 carbon atoms, preferably a n-butyl group, and X^- as the monovalent anion is preferably BF_4^- , PF_6^- , ClO_4^- , or SbF_6^- .

10 A diimmonium compound in which R is a butyl group and X^- is SbF_6^- represented by the following formula (V):

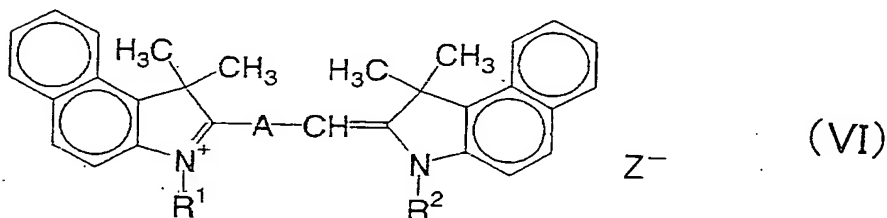


[0018] The near-infrared absorption layer may contain only

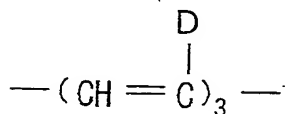
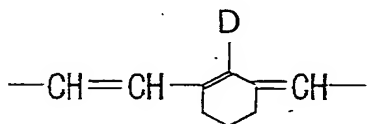
one or two or more of the aforementioned diimmonium compounds. The near-infrared absorption layer preferably contains about 0.1% to 10% by weight of diimmonium compound.

[0019] The near-infrared absorption layer may contain another compound besides the diimmonium compound. Such compound may be a cyanine compound, a phthalocyanine compound, a naphthalocyanine compound, a nickel complex compound, and/or a quencher compound.

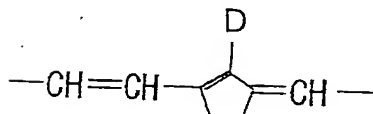
[0020] The cyanine compound may be a compound represented by the following formula (VI):



[0021] In the formula (VI), A is a divalent bonded group containing an ethylene group. Particularly preferable cyanine compound is:

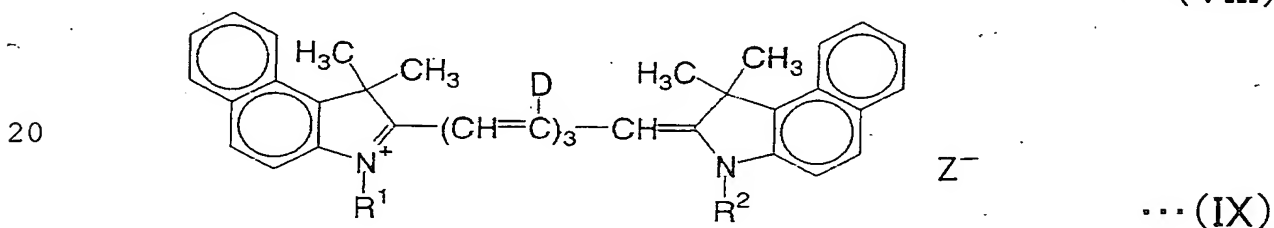
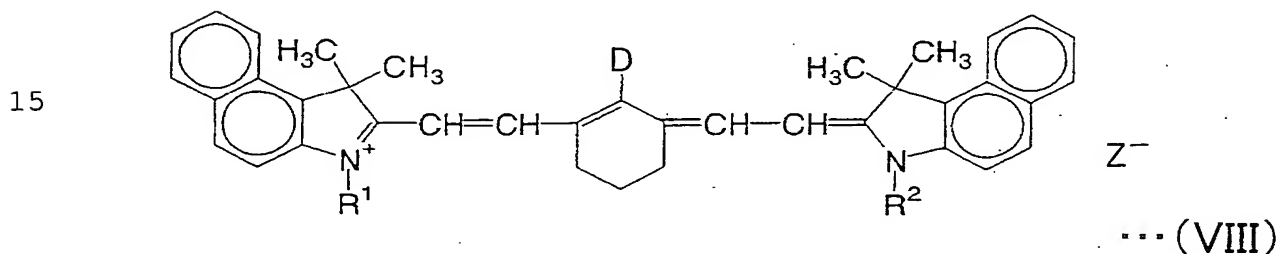
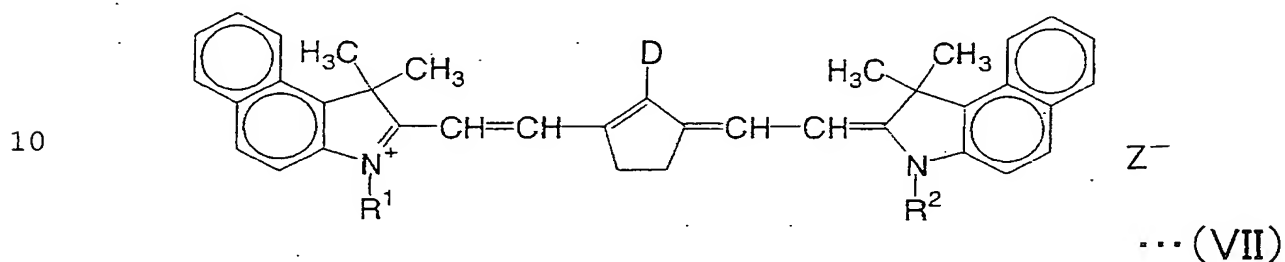


or



(D is one of an alkyl group, diphenyl amino group, a halogen atom, and hydrogen atom). That is, specific examples of the cyanine compound represented by the formula (VI) are represented by the following formulae (VII), (VIII), and (IX).

5 The cyanine compound has a function of making the transmittance for visible light and the color of the near-infrared absorption layer better.



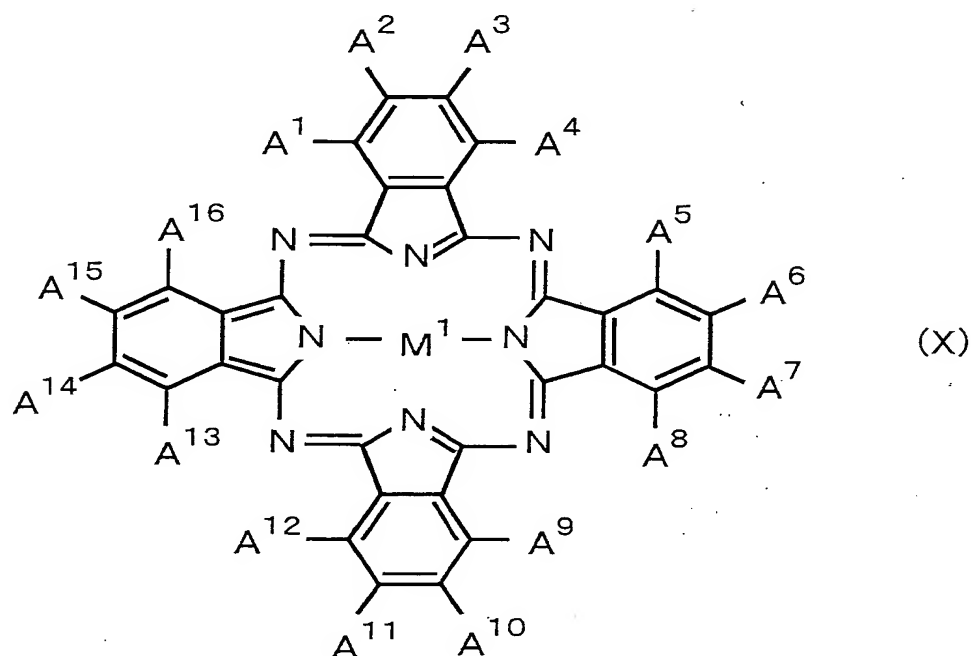
[0022] In the formulae (VI) through (IX), each of R¹ and R² is a monovalent group having a carbon atom and may be an alkyl group, an aryl group, an alkoxy group, an alkoxy carbonyl group, a sulfonyl alkyl group, or a cyano group. Z⁻ is a monovalent anion and may be I⁻, Br⁻, ClO₄⁻, or BF₄⁻, PF₆⁻, SbF₆⁻, CH₃SO₄⁻, NO₃⁻, or CH₃-C₆H₄-SO₃⁻.

[0023] The near-infrared absorption layer may contain 50 parts by weight or less, preferably from 0.1 to 50 parts by

weight, more preferably from 1 to 50 parts by weight of the cyanine compound relative to 100 parts by weight of the aforementioned diimmonium compound.

[0024] When the content is 0.1 parts by weight or more, the cyanine compound can exhibit its function of improving the blocking performance against near-infrared rays. On the other hand, when the content exceeds 50 parts by weight, the cyanine compound may make the transmittance of visible light poor.

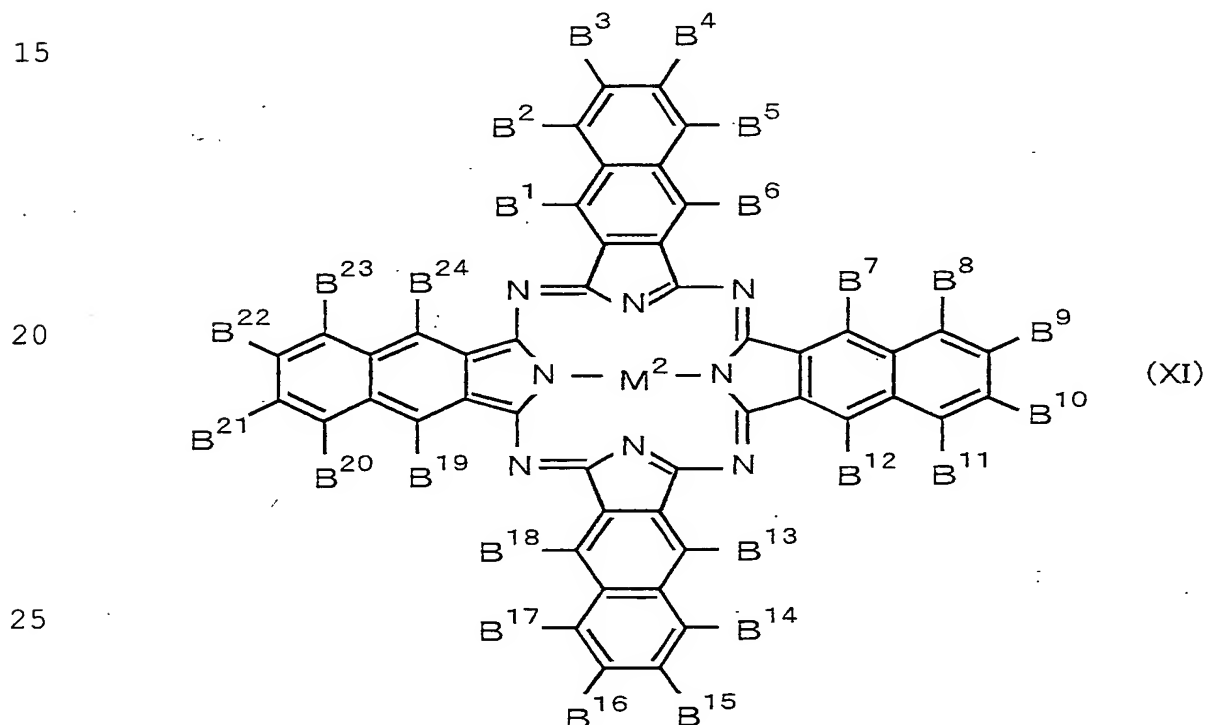
[0025] The phthalocyanine compound which can be contained in the near-infrared absorption layer may be a compound represented by the following formula (X):



[0026] In the formula (X), A¹ through A¹⁶ each represent independently either one of the followings, i.e. a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, a hydroxysulfonyl group, an aminosulfonyl group, or a

substituent having from 1 to 20 carbon atoms. The substituent having from 1 to 20 carbon atoms may contain either one of the followings, i.e. a nitrogen atom, a sulfur atom, an oxygen atom, and a halogen atom. Adjacent two substituents may be bonded to each other via a conjugating group. Each of at least four of A¹ through A¹⁶ is at least either one of a substituent via sulfur atom and a substituent via nitrogen atom. M¹ is either one of the followings, i.e. two hydrogen atoms, a divalent metallic atom, a trivalent or quadrivalent substituted metallic atom, and an oxy metal.

[0027] The naphthalocyanine compound which can be contained in the near-infrared absorption layer may be a compound represented by the following formula (XI):



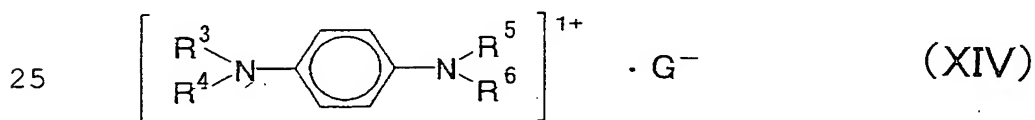
[0028] In the formula (XI), B¹ through B²⁴ each represent independently either one of the followings, i.e. a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, a

hydroxysulfonyl group, an aminosulfonyl group, or a substituent having from 1 to 20 carbon atoms. The substituent having from 1 to 20 carbon atoms may contain a nitrogen atom, a sulfur atom, an oxygen atom, and a halogen atom. Adjacent two substituents may be bonded to each other via a conjugating group. Each of at least four of B¹ through B²⁴ is at least either one of a substituent via oxygen atom, a substituent via sulfur atom, a substituent via nitrogen atom. M² is either one of the followings, i.e. two hydrogen atoms, a divalent metallic atom, a trivalent or quadrivalent substituted metallic atom, and an oxy metal.

[0029] The quencher compound which can be contained in the near-infrared absorption layer may be a metallic compound represented by the following formula (XII) or (XIII), or an aminium compound represented by the following formula (XIV):



[0030] In the formulae (XII) and (XIII), M is Ni, Cu, Co, Pt, or Pd.

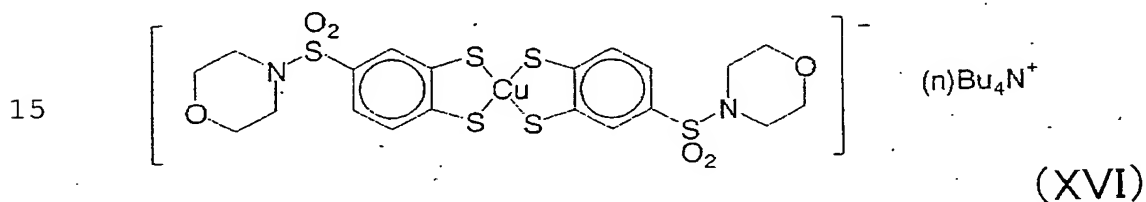
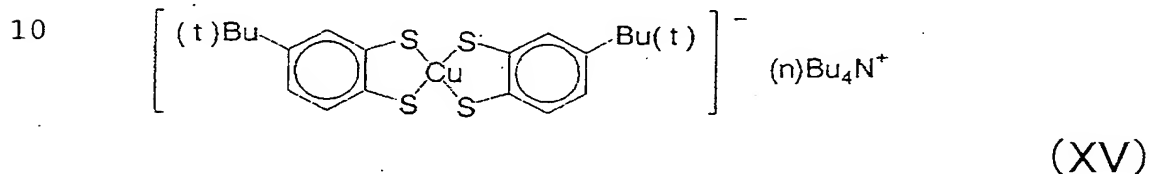


[0031] In the formula (XIV), each of R³ through R⁶ is at least one selected from a group consisting of an alkyl group, an aryl group, a group having aromatic ring, a hydrogen atom, and a halogen atom, and G⁻ is I⁻, Br⁻, ClO₄⁻, or BF₄⁻, PF₆⁻,

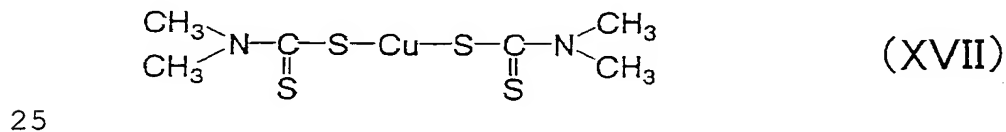
SbF_6^- , CH_3SO_4^- , NO_3^- , or $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3^-$.

[0032] The metallic compound represented by the formula (XII) may be a 1,2-benzenethiol copper complex compound or a 1,2-benzenethiol nickel complex compound. Specific

5 examples are compound represented by formulae (XV) and (XVI). These compounds can exhibit a function of preventing the oxidization of the near-infrared absorption layer so as to improve the durability of the near-infrared absorption layer. (t)Bu means a t-butyl group and (n)Bu means a n-butyl group.



[0033] The metallic compound represented by the formula (XIII) may be a complex represented by the following formula (XVII). This complex can exhibit a function of preventing the oxidization of the near-infrared absorption layer so as to improve the durability of the near-infrared absorption layer.



[0034] The near-infrared absorption layer may contain 100 parts by weight or less, preferably from 0.01 to 100 parts by weight, more preferably from 0.1 to 50 parts by weight of the quencher compound relative to 100 parts by weight of

the diimmonium compound.

[0035] Though the quencher compound can exhibits its function of improving the durability such as heat resistance, oxidation resistance and moisture resistance, the quencher
5 compound can color the near-infrared absorption layer so as to make the appearance of the near-infrared absorption layer poor.

[0036] The nickel complex compound which can be contained in the near-infrared absorption layer has a function of
10 absorbing near-infrared rays.

[0037] The near-infrared absorption layer may further contain other components, for example, a binder resin, a near-infrared absorbent (e.g. near-infrared absorbents of
15 azo series, polymethine series, diphenylmethane series, triphenylmethane series, and quinine series), an antioxidant other than the quencher compound (e.g. antioxidants of phenol series, amine series, hindered bisphenol series, hindered amine series, sulfur seires, phosphoric acid series, phosphorous acid series, and metallic complex series), an
20 UV absorbent, and a colorant, a pigment, and a dye for improving the appearance of the film.

[0038] The binder resin may be polyester resin, acrylic resin, methacrylic resin, urethane resin, silicone resin, phenol resin, or a homopolymer or copolymer of (meth) acrylic
25 acid ester. Among these, acrylic resin or polyester resin may be preferably used from the viewpoints of dispersibility of the diimmonium compound and the durability.

[0039] The thickness of the near-infrared absorption layer may be from 0.5 μm to 50 μm . Though the thickness in this range
30 is better for the near-infrared absorption and transmittance

for visible light, the thickness is not limited thereto.

[0040] The base film is made of a synthetic resin and may be made of polyolefine resin such as polyethylene and polypropylene, polyester resin, acrylic resins, cellulose resin, polyvinylchloride resin, polycarbonate resin, phenol resin, or urethane resin. Among these, polyester resin is preferable because of high transparency and lower risk of environmental pollution. The transparency means the transparency relative to visible light.

10 [0041] The thickness of the base film may be from 50 μm to 200 μm . The thickness in this range can impart sufficient mechanical strength to the base film.

[0042] Coating liquid is prepared by dissolving the diimmonium compound, the binder resin, and the like into a solvent and is coated on the base film, thereby manufacturing the near-infrared absorption film. The solvent may be dichloromethane, methyl ethyl ketone, tetrahydrofuran, or cyclohexanone.

15 [0043] The near-infrared absorption film may have one near-infrared absorption layer or two or more near-infrared absorption layers on the base film.

[0044] The near-infrared absorption film as described in the above can sufficiently absorb near-infrared rays and transmit visible light of wavelengths in a wide range. Since the film has excellent durability, particularly excellent durability in high-temperature and high-humidity conditions, the film can be adopted to various applications.

Examples

30 [0045] Hereinafter, examples of the present invention will

be described. The present invention is not limited to the following examples.

Examples 1-4, Comparative Examples 1-4

5 [Production of Near-infrared Absorption Film]

[0046] Diimmonium compound (CIR1081; available from Japan Carlit Co., Ltd.) represented by the aforementioned formula (V) was refined. By raising the purity step by step during the refining process, refined diimmonium compounds of three
10 kinds with different purities were obtained. As for each of the obtained diimmonium compounds, 1 mg was weighed in a cell made of aluminum and the temperature at heat absorption peak (melting point) was measured by a differential scanning calorimeter (DSC-3100; available from MAC Science Co., Ltd.).
15 The results were 227°C, 220°C, and 210°C, respectively. The temperature rising rate during the measurement was 10°C/minute. The melting point of CIR1081 diimmonium compound mentioned above was measured and the result was 207°C.

[0047] Each diimmonium compound and each binder resin
20 indicated in Table 1 were dissolved in the respective amounts indicated in Table 1 into a mixed solvent consisting of 18.5g of dichloromethane, 55.5g of tetrahydrofuran, and 18.5 of methyl cellosolve acetate, thereby preparing each coating liquid. The coating liquid was coated on a polyester film
25 ("T600E/W07" having a thickness of 100 µm; available from Mitsubishi Polyester Film Corporation) by using a bar coater and was then dried at 100°C for three minutes so as to form a near-infrared absorption film having a near-infrared absorption layer of 5 µm in thickness when dried.

30 [Durability Evaluation]

[0048] The peak in absorbency of the obtained near-infrared absorption film was measured by a spectrophotometer (U-4000; available from Hitachi Instruments Service Co., Ltd.) and the result was used as initial absorbency I_0 . Then, the absorbencies were measured after leaving the obtained near-infrared absorption film for 500 hours at 80°C and 60%RH and for 500 hours at 60°C and 90%RH, respectively. The results were each used as absorbency I_{500} . The residual ratio (%) of the diimmonium compound was calculated according to the following equation. The durability was evaluated such that the film in which the residual ratio of diimmonium compound was 92% or more was valued as "excellent" when, the film in which the residual ratio of diimmonium compound was 90% or more and less than 92% was valued as "good", and the film in which the residual ratio of diimmonium compound was less than 90% was valued as "NG". The results were shown in Table 2.

$$\text{Residual ratio of diimmonium compound(\%)} = I_{500}/I_0$$

Table 1

	Near-infrared Absorbent			Binder Resin		
	Compound	Melting Point (°C)	Amount (g)	Compound	Trade name	Amount (g)
Example 1	Diimmonium compound	227	0.4	Polyester resin	UE3690	7.5
Example 2	Diimmonium compound	220	0.4	Polyester resin	UE3690	7.5
Example 3	Diimmonium compound	227	0.4	PMMA	80N	7.5
Example 4	Diimmonium compound	220	0.4	PMMA	80N	7.5
Comparative Example 1	Diimmonium compound	210	0.4	Polyester resin	UE3690	7.5
Comparative Example 2	Diimmonium compound	207	0.4	Polyester resin	UE3690	7.5
Comparative Example 3	Diimmonium compound	210	0.4	PMMA	80N	7.5
Comparative Example 4	Diimmonium compound	207	0.4	PMMA	80N	7.5

Note: "UE3690" is a polyester resin (Elytel UE3690; available from Unitika Ltd.)

"80N" is polymethyl methacrylate (PMMA resin) (Delpet 80N; available from Asahi Kasei Chemicals Corporation)

Table 2

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Residual ratio of diimmonium compound	After 500 hours at 80°C and 60%RH 94.7%	After 500 hours at 80°C and 60%RH 93.9%	After 500 hours at 80°C and 60%RH 92.7%	After 500 hours at 80°C and 60%RH 90.5%	After 500 hours at 80°C and 60%RH 85.4%	After 500 hours at 80°C and 60%RH 84.2%	After 500 hours at 80°C and 60%RH 86.1%	After 500 hours at 80°C and 60%RH 81.4%
	After 500 hours at 60°C and 90%RH 95.2%	After 500 hours at 60°C and 90%RH 91.0%	After 500 hours at 60°C and 90%RH 93.0%	After 500 hours at 60°C and 90%RH 91.0%	After 500 hours at 60°C and 90%RH 86.2%	After 500 hours at 60°C and 90%RH 83.8%	After 500 hours at 60°C and 90%RH 76.2%	After 500 hours at 60°C and 90%RH 69.1%
Evaluation	Excellent	Excellent	Excellent	Good	NG	NG	NG	NG
	Excellent	Good	Excellent	Good	NG	NG	NG	NG

[0049] It is found from Table 2 that any one of Examples 1 through 4 has better durability as compared to Comparative Examples 1 through 4.

[0050] As described in the above, the present invention can
5 provide a near-infrared absorption film which is excellent in blocking property against near-infrared rays, in transmittance to visible light within a wider range of wavelength, and also in durability.